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# Investigation on hydrogen production by catalytic steam reforming of maize stalk fast pyrolysis bio-oil

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## ABSTRACT

Hydrogen production via catalytic steam reforming of maize stalk fast pyrolysis bio-oil over the nickel/alumina supported catalysts promoted with cerium was studied using a laboratory scale fixed bed coupled with Fourier transform infrared spectroscopy/thermal conductivity detection analysis (FTIR/TCD). The effects of nickel loading, reaction temperature, water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity ( $W_bHSV$ ) on hydrogen production were investigated. The highest hydrogen yield of 71.4% was obtained over the 14.9%Ni-2.0%Ce/ $Al_2O_3$  catalyst under the reforming conditions of temperature = 900 °C, WCMR = 6 and  $W_bHSV$  = 12 h<sup>-1</sup>. Increasing reaction temperature from 600 to 900 °C resulted in the significant increase of hydrogen yield. The hydrogen yield was significantly enhanced by increasing the WCMR from 1 to 3, whereas it increased slightly by further increasing WCMR. The hydrogen yield decreased with the increase of  $W_bHSV$ . Meanwhile, the coke deposition percentage changed little with increasing  $W_bHSV$  up to 12 h<sup>-1</sup> and then it increased by 4.5% with the further increase of  $W_bHSV$  from 12 to 24 h<sup>-1</sup>.

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## Introduction

Nowadays, there is a growing interest in the utilization of hydrogen as an environmentally friendly and efficient energy carrier for power generation coupled with fuel cell systems. Moreover, hydrogen is an important chemical raw material and widely used in the chemical, fertilizer, food, petrochemical and metallurgical industries [1]. Currently hydrogen is mainly produced by catalytic steam reforming of fossil fuels

such as coal, natural gas, naphtha and heavy oils [2]. Considering both the growing shortage of fossil fuels and the worsening of ecological environment, hydrogen production from bio-oil produced by fast pyrolysis of biomass as a renewable energy source has attracted more and more attention all over the world.

The bio-oil catalytic steam reforming technology for hydrogen production has the following advantages: (1) The biomass fast pyrolysis technology for bio-oil production has been extensively studied and made great progress in the past

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twenty years, which provides technical support for the effective mass production of bio-oil; (2) The liquid bio oil has significantly higher energy density and is much easier to collect, store and transport than solid biomass, which solve the problems of the large-scale collection, storage and transportation of biomass raw materials; (3) This technology gives hydrogen-rich gas and high value-added by-products, which can improve the economy of the entire process. Therefore, the bio-oil catalytic steam reforming technology is one of the most promising approaches to produce hydrogen from biomass on an industrial scale.

At present, the research progress in bio-oil catalytic steam reforming for hydrogen generation remains very slow. This is mainly attributed to the complexity of biomass pyrolysis oil composition. The existing most studies have focused on catalytic steam reforming of bio-oil aqueous fraction [3–6] and model compounds such as acetic acid [7], acetone [8], acetol [9], butanol [9], ethylene glycol [10] and m-cresol [11] over different catalysts. It is worth noting that the energy yield decreases when bio-oil aqueous fraction is catalytically reformed by the steam, due to the requirement of the primary separation process [12]. With respect to this issue, hydrogen production from crude bio-oil is a viable option.

However, the studies on steam reforming of bio-oil itself for hydrogen generation are very limited and the existing studies have mainly focused on hydrogen production via steam reforming of bio-oil itself in a two-step process. Kan et al. [13] investigated catalytic steam reforming of corn stalk pyrolysis bio-oil over the NiCuZnAl catalyst in the gasification-reforming dual beds. The maximum hydrogen yield of 81.4% with carbon conversion of 87.6% was achieved through the integrative gasification-reforming process. Wu et al. [14] studied catalytic steam reforming of sawdust pyrolysis bio-oil for hydrogen production in a two-stage fixed bed reactor system. They chose dolomite in the first steam reforming stage for the conversion of bio-oil and Ni/MgO in the second stage for the conversion of methane to increase the hydrogen purity and yield. Davidian et al. [15] employed a sequential catalytic cracking/reforming process for hydrogen generation from beech wood pyrolysis oil over the Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-K/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts and obtained a hydrogen-rich gas mixture in which the hydrogen concentration was 45–50%. Domine et al. [16] studied hydrogen production from biomass-derived oil over monolithic platinum- and rhodium-based catalysts using steam reforming and sequential cracking processes. They reported that the highest hydrogen yield was 70% with the Pt catalyst at 780 °C and an S/C ratio of 10. To the best of our knowledge, few studies have been performed on the catalytic steam reforming of crude bio-oil in a one-stage process for hydrogen production, particularly for maize stalk fast pyrolysis bio-oil.

In the present study, hydrogen production via catalytic steam reforming of maize stalk fast pyrolysis bio-oil over the nickel/alumina supported catalysts promoted with cerium was studied using a laboratory scale fixed bed coupled with Fourier transform infrared spectroscopy/thermal conductivity detection analysis (FTIR/TC). The effect of various influential parameters such as nickel loading, reaction temperature, water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity (W<sub>b</sub>HSV) on the hydrogen production were also analyzed herein.

## Experimental

### Bio-oil feedstock

The bio-oil used in this work was obtained by fast pyrolysis of maize stalk in a fluidized-bed biomass fast pyrolysis liquefaction plant located in Shandong Research Center of Engineering & Technology for Clean Energy (Zibo, China). The pyrolysis of maize stalk was performed at 540–550 °C with a heating rate of about 10<sup>3</sup> °C/s for a residence time of less than 2 s. The elemental composition of bio-oil was analyzed using a Euro EA3000 elemental analyzer. The water content of bio-oil was determined by the Karl–Fischer method [17] using Metrohm-870 KF Titrino plus Karl–Fischer titrator. Before the measurement, a Karl–Fischer reagent (Hydranal Composite 5) was used as a titrant and standardized with deionized distilled water. The calorific value was obtained using an IKA C2000 automatic isoperibol calorimeter. The pH value was measured by a PHS-2F digital pH meter. Prior to the measurement, the instrument was calibrated with a liquid calibration standard of pH 7. The density of bio-oil was measured using a density measurement bottle. The gas chromatography/mass spectrometry (GC/MS) analysis of bio-oil was conducted using an Agilent 6890/5973N Gas Chromatograph–Mass Spectrometer.

### Catalysts preparation and characterization

Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and aluminum oxide (γ-Al<sub>2</sub>O<sub>3</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. A series of Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with different nickel loadings were prepared by co-impregnation using the aqueous solution of nickel nitrate and cerium nitrate supported on alumina. The γ-Al<sub>2</sub>O<sub>3</sub> was first pretreated at 650 °C for 6 h and then crushed to 60–80 mesh. Known amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved in deionised water and the pretreated γ-Al<sub>2</sub>O<sub>3</sub> was added to the solution. The obtained slurry was continuously stirred at room temperature for 3 h, then dried at 110 °C for 48 h in a drying oven and subsequently calcined at 600 °C for 4 h in a muffle furnace. The metallic element contents in the prepared catalysts were measured by the inductively coupled plasma atomic emission spectroscopy (ICP/AES) using a TraceScan Advantage™ equipment (Thermo Jarrell Ash Corporation). Four catalysts were obtained: 5.1%Ni-2.0%Ce/Al<sub>2</sub>O<sub>3</sub>, 10.3%Ni-2.0%Ce/Al<sub>2</sub>O<sub>3</sub>, 14.9%Ni-2.0%Ce/Al<sub>2</sub>O<sub>3</sub> and 20.4%Ni-2.0%Ce/Al<sub>2</sub>O<sub>3</sub>, which were labeled as NiCe-1, NiCe-2, NiCe-3 and NiCe-4, respectively.

The Brunauer–Emmett–Teller (BET) surface area and pore structural characteristics of the catalysts were evaluated by using a Micromeritics TriStar 3000 gas absorption analyzer. Before the nitrogen physisorption experiments, the samples were preheated according to the method provided by the literature [18]. The catalyst crystallographic structure was determined by X-ray diffraction (XRD). The XRD patterns were obtained using a Bruker AXS D8 Advance X-Ray Diffractometer with Cu Kα radiation of wavelength 0.154 nm at 40 kV and 35 mA. The data were recorded from a start angle of 10° to an end angle of 70°.

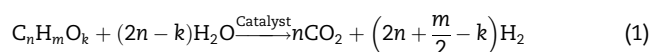
### Experimental apparatus and procedure

The bio-oil catalytic steam reforming experiments were carried out in the experimental setup shown in Fig. 1. Two high-pressure syringe pumps were used to feed bio-oil and water to the fixed bed reactor. The quartz tube reactor with an inner diameter of 10 mm and length of 450 mm was heated by the carborundum heater with the well-programmed temperature control. A chromel/alumel thermocouple was placed inside the catalyst bed in the middle of the reactor to measure the reaction temperature. The gas analysis system consisted of a Gasboard-3100 gas analyzer and a Gasmet Dx-4000 FTIR multicomponent gas analyzer. The former was equipped with the proprietary non-dispersive infrared gas sensor and thermal conductivity detector and could quantify  $H_2$ , CO,  $CO_2$  and  $CH_4$ . The latter allowed a quantitative analysis of CO,  $CO_2$ ,  $CH_4$ , ethane, ethylene, propane, etc. Before each experiment the catalysts were reduced in situ with a 50 vol%  $H_2/N_2$  mixture (flow rate 50 mL/min) at 600 °C for 2 h. The reactor was then purged with purified nitrogen ( $\geq 99.995\%$ ) at a flow rate of 50 mL/min for 1 h and heated up to the desired temperature in the temperature range of 600–900 °C. Afterwards, bio-oil and steam were introduced into the reaction system by the two high-pressure syringe pumps which could control their feed rates. The produced gases were passed through two successive ice-cooled condensers at about 0 °C to mostly separate the excess water and some unconverted bio-oil. The cotton wool filter was used to capture the residual condensable vapors to reduce the interference to the rear gas analysis instrument as far as possible. The clean gases were dried by a silica gel filter, swept immediately to the Gasboard-3100 gas analyzer via a Teflon tube, then to the Gasmet Dx-4000 FTIR multicomponent gas analyzer. After each experiment, the catalyst bed was swept and cooled in a nitrogen flow to room

temperature. Subsequently, the catalyst bed including the condensers, pipelines and the silica gel filter were removed and weighted for the following analysis. Finally, the air was introduced into the reactor to remove the heavy tar on the pipe wall by combustion method. The condensers and all possible condensate pipelines were cleaned by acetone and the solvent was evaporated under the constant temperature of 60 °C.

### Data analysis

The overall catalytic steam reforming reaction of bio-oil for hydrogen production could be simply represented by the Eq. (1). It can be seen that hydrogen is derived not only from the bio-oil but also from the steam.



The catalytic performances of the catalysts were evaluated in terms of hydrogen, carbon monoxide, carbon dioxide, methane and ethane yields. The hydrogen yield was defined as the ratio of the number of moles of produced hydrogen to the theoretical maximum quantity of the hydrogen corresponding to the complete steam reforming of bio-oil to  $CO_2$  and  $H_2$  and calculated by the Eq. (2). The yields of the other gases were calculated by the Eq. (3). The carbon conversion could be obtained by the sum of the moles of carbon in the gaseous products divided by the moles of carbon fed. Coke deposition percentage was defined by the Eq. (4). The water to carbon molar ratio (WCMR) and bio-oil weight hourly space velocity ( $W_bHSV$ ) were defined by the Eqs. (5) and (6), respectively. It is worth noting that the WCMR mentioned here did take into account the water present in the bio-oil.

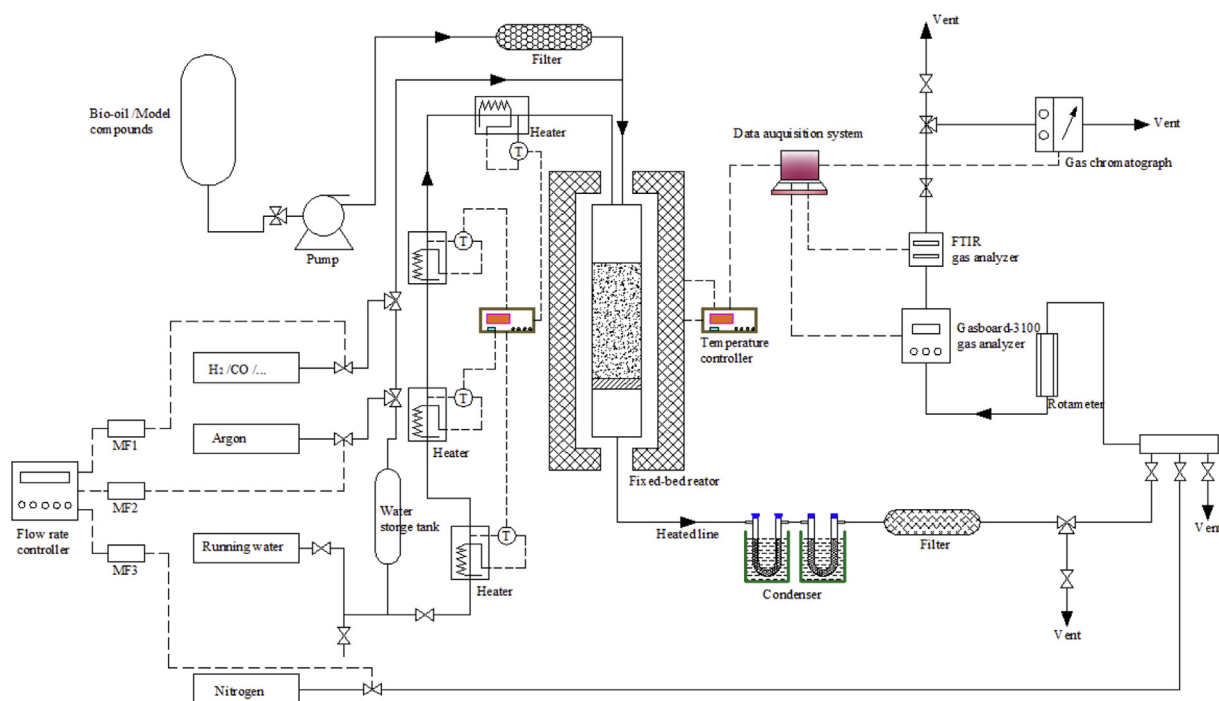


Fig. 1 – Schematic diagram of the bio-oil catalytic steam reforming experimental system.

$$\text{H}_2 \text{ yield } (\%) = \frac{\text{moles of hydrogen produced}}{\left(2n + \frac{m}{2} - k\right) \times \text{moles of carbon fed}/n} \times 100 \quad (2)$$

$$\text{Other gas yield } (\%) = \frac{\text{moles of gas produced}}{\text{moles of carbon fed}} \times 100 \quad (3)$$

$$\text{Coke deposition } (\%) = \frac{\text{weight of coke deposited on the catalyst bed}}{\text{weight of bio-oil fed}} \times 100 \quad (4)$$

$$\text{WCMR} = \frac{\text{moles of total water fed}}{\text{moles of carbon fed}} \quad (5)$$

$$\text{W}_b\text{HSV}(\text{h}^{-1}) = \frac{\text{mass flow rate of bio-oil}}{\text{mass of catalyst}} \quad (6)$$

## Results and discussion

### The properties and compositions of bio-oil

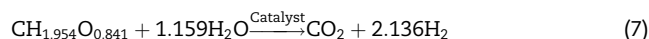
The bio-oil produced from fast pyrolysis of maize stalk was a viscous and dark-brown organic liquid with a fairly strong smoky odour. Table 1 gives some physical and chemical properties of the bio-oil used. The main elemental composition of the bio-oil is carbon, hydrogen and oxygen, whose contents are 43.6%, 7.1% and 48.9%, respectively. The bio-oil can be described by the average chemical formula of  $\text{CH}_{1.954}\text{O}_{0.841}$  on the basis of the elemental composition. Moreover, the bio-oil also contains a small amount of nitrogen and traces of metals like potassium, magnesium and calcium, which have not been analyzed here. The oxygen content of the bio-oil is high due to the presence to oxygenated compounds such as acids, aldehydes, ketones, esters, alcohols and phenols, etc. and also partly due to the high water content, leading to high viscosities and boiling points as well as relatively poor chemical stability. The calorific value of the bio-oil is 17.2 MJ/kg and much lower than those of some conventional liquid fuels such as diesel and gasoline [19]. This is mainly due to its high oxygen content. The density of the bio-oil was

1220 kg/m<sup>3</sup> and much higher than that of maize stalk. This means that the bio-oil has much higher energy density compared to maize stalk and is more convenient for storage, transportation and utilization.

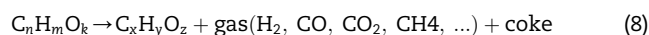
The main organic components of the bio-oil were identified with GC/MS technique. Fig. 2 shows the total ion current chromatogram of maize stalk fast pyrolysis bio-oil. It can be found

that more than 100 peaks were displayed in the chromatogram. Most of the identified peaks are oxygenated compounds, which included acids, aldehydes, ketones, esters, alcohols, furanics, pyranics, anhydrosugars and phenols, etc. Since the oxygenated compounds in the bio-oil are nonpolar, it is not miscible with petroleum oil. Nevertheless, the bio-oil could be blended with petroleum fuel via emulsification. Table 2 lists the major chemical compounds in maize stalk fast pyrolysis bio-oil as determined by GC/MS. The major chemical compounds includes 1-hydroxy-2-propanone, acetic acid, ethanol, 1,2-Ethandiol, 2-Methyl-2-cyclopenten-1-one, benzenediol, levoglucosan and phenols, etc. The perfect identification of all the peaks is not possible due to the complex composition of biomass pyrolysis oil and the difficulties in the identification are mainly due to overlapping peaks and low signal to noise ratios.

In the case of the bio-oil ( $\text{CH}_{1.954}\text{O}_{0.841}$ ) used in this research, the overall stoichiometric steam reforming reaction can be expressed as follows:



This means that the theoretical maximum hydrogen yield is 0.1558 g H<sub>2</sub> g<sup>-1</sup><sub>bio-oil</sub> for the bio-oil used in this study, only when the bio oil is completely reformed into hydrogen and carbon dioxide. However, in fact the hydrogen yield is difficult to reach the theoretical maximum due to some accompanied side reactions [20], such as the thermal decomposition (Eq. (8)), methanation (Eqs. (9) and (10)) and boudouard (Eq. (11)) reactions, etc.



### Catalyst characterization

#### Characteristics of the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts

The BET surface area, pore volume, and average pore size of the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with different Ni loadings are shown in Table 3. As the nickel loading increases from 5.1% to 20.4%, the BET surface area and total pore volume gradually decrease from 149.5 m<sup>2</sup>/g and 0.69 cm<sup>3</sup>/g to 101.9 m<sup>2</sup>/g and 0.35 cm<sup>3</sup>/g,

**Table 1 – The main properties of bio-oil derived from fast pyrolysis of maize stalk.**

Properties	
Elemental composition (wt%)	
Carbon	43.6
Hydrogen	7.1
Nitrogen	0.4
Oxygen (by difference)	48.9
Water content (wt%)	23.5
Density (kg/m <sup>3</sup> )	1220
Calorific value (MJ/kg)	17.2
pH	3.2

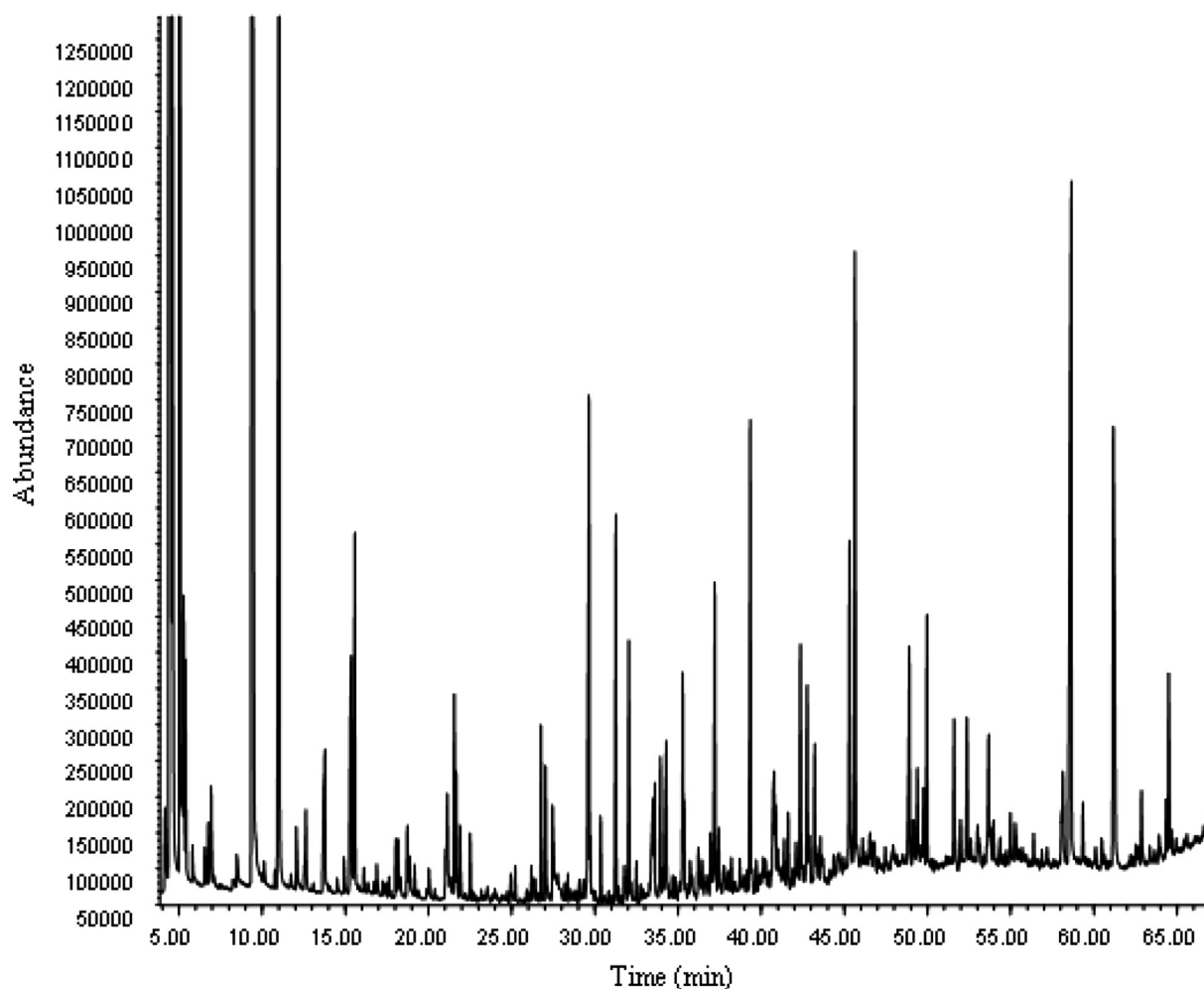


Fig. 2 – The total ion current chromatogram of maize stalk fast pyrolysis bio-oil.

Table 2 – Major chemical compounds in maize stalk fast pyrolysis bio-oil as determined by GC–MS.

No.	Retention time (min)	Compound name
1	5.044	Ethanol
2	9.433	Acetic acid
3	11.048	2-Propanone, 1-hydroxy-
4	15.358	1,2-Ethanediol
5	21.142	2-Furanmethanol
6	21.564	2-Propanone, 1-(acetyloxy)-
7	21.681	2-Cyclopenten-1-one, 2-methyl-
8	21.913	1,2-Ethanediol, monoacetate
9	22.507	Ethanone, 1-(2-furanyl)-
10	27.055	Butanoic acid, 4-hydroxy-
11	32.049	Phenol, 2-methoxy-
12	33.604	Phenol, 2-methyl-
13	33.953	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-
14	34.296	Cyclobutane methanol
15	37.215	Cyclopropyl carbinol
16	39.352	Phenol, 4-ethyl-
17	42.773	Xanthosine1,
18	45.313	2-Benzenediol
19	49.97	Hydroquinone
20	51.600	3,5-Dihydroxytoluene
21	58.65	1,6-Anhydro- $\alpha$ -D-glucopyranose (levoglucosan)



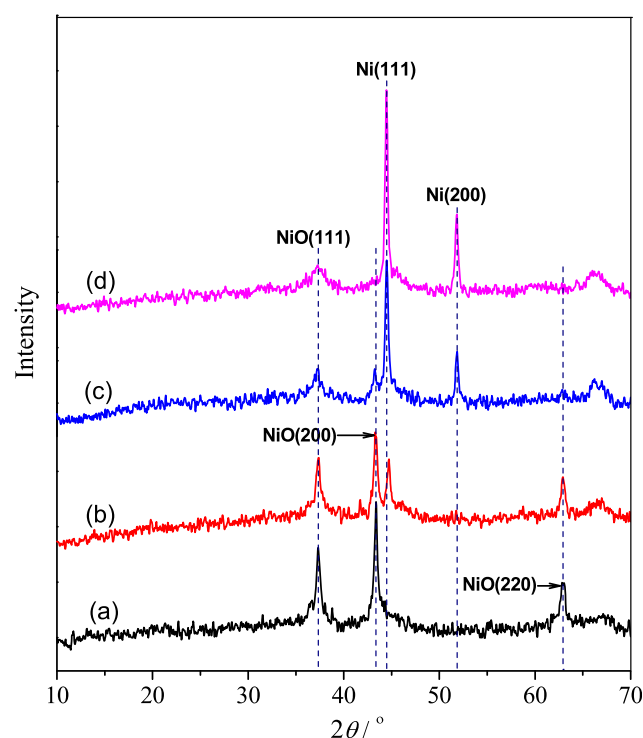
**Table 3 – Characteristics of the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with different Ni loadings.**

Catalyst	Ni content (%)	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)
NiCe-1	5.1	149.5	0.69	13.65
NiCe-2	10.3	138.3	0.63	14.17
NiCe-3	14.9	114.6	0.51	13.39
NiCe-4	20.4	101.9	0.35	10.52

respectively. The above results suggest a negative effect of adding nickel on the pore structure properties in the catalysts. The impregnated nickel species may be mainly located on the inner surface of the pores of the alumina support and high nickel loadings can result in the aggregation of the nickel and/or blockage of the catalyst pores, which leads to the decrease of the BET surface area with increasing the nickel content.

#### XRD analysis

The catalyst crystalline structure was determined by X-ray diffraction. The XRD diffraction patterns of the fresh NiCe-3 catalyst and the used catalysts under steam reforming for 1 h at different temperatures are presented in Fig. 3. The three bands in the XRD pattern of the fresh catalyst are clearly observed at  $2\theta = 37.3^\circ$ ,  $43.3^\circ$  and  $62.9^\circ$  as shown in Fig. 3 (a). As reported by Li et al. [13], the three bands at  $2\theta = 37.3^\circ$ ,  $43.3^\circ$  and  $62.9^\circ$  correspond to the NiO(111), NiO(200) and NiO(220) peaks. The XRD pattern of the catalyst after reforming reactions at  $600^\circ\text{C}$  is presented in Fig. 3 (b). A new diffraction peak appears at  $2\theta = 44.7^\circ$ , corresponding to the Ni(111) peak [21].



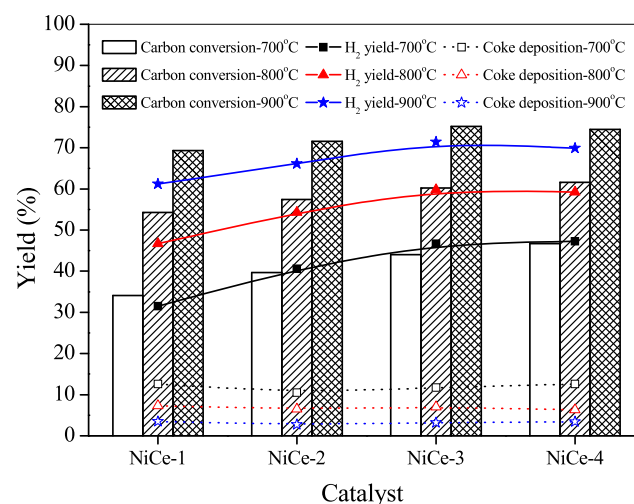
**Fig. 3 – XRD diffraction patterns of (a) the fresh NiCe-3 catalyst and the used NiCe-3 catalysts under steam reforming for 1 h at different temperatures: (b)  $600^\circ\text{C}$ , (c)  $700^\circ\text{C}$  and (d)  $800^\circ\text{C}$ .**

Furthermore, the intensities of the three bands at  $2\theta = 37.3^\circ$ ,  $43.3^\circ$  and  $62.9^\circ$  gradually decrease. The above results indicate that a certain amount of NiO within the catalyst is reduced to metallic Ni, which is conducive to enhance the catalyst activity. When the reforming temperature rises to  $700^\circ\text{C}$ , the Ni(111) peak intensity significantly increases. Meanwhile, a new diffraction band appears at  $2\theta = 51.8^\circ$ , corresponding to the Ni(200) peak [21]. These suggest that the reduction degree of NiO within the catalyst increases and higher temperatures is favorable for the reduction of more NiO within the catalyst to Ni. As the reaction temperature further increases to  $800^\circ\text{C}$ , the intensities of the two bands at  $2\theta = 44.5^\circ$  and  $51.8^\circ$  become greater and the reduction degree of NiO within the catalyst further increases. The reduction from  $\text{Ni}^{2+}$  to  $\text{Ni}^0$  should be attributed to the reaction of  $\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O}$ , where hydrogen was produced by the gasification of the crude bio-oil and the organic intermediates reforming. It is noteworthy that higher temperature results in the higher reduction level of the NiCe-3 catalyst, which indicates that high temperature is favorable to improve the catalytic activity of the nickel/alumina supported catalysts promoted with cerium. However, the reaction temperature should not be too high, because excessive reaction temperature can lead to the agglomeration and sintering of particles and thus the catalyst deactivation.

#### Steam reforming of the bio-oil

##### Effect of nickel loading

Fig. 4 compares the catalytic activity of the four Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts at various temperatures in terms of hydrogen yield, carbon conversion and coke deposition percentage. The hydrogen yield first significantly increases with increasing the nickel loading and then slightly increases with the further increase in the nickel loading. The carbon conversion shows the similar trend to the hydrogen yield. From the point of view of both hydrogen yield and carbon conversion, the NiCe-1 catalyst is less effective than the other three catalysts. Although the other three catalysts have different nickel

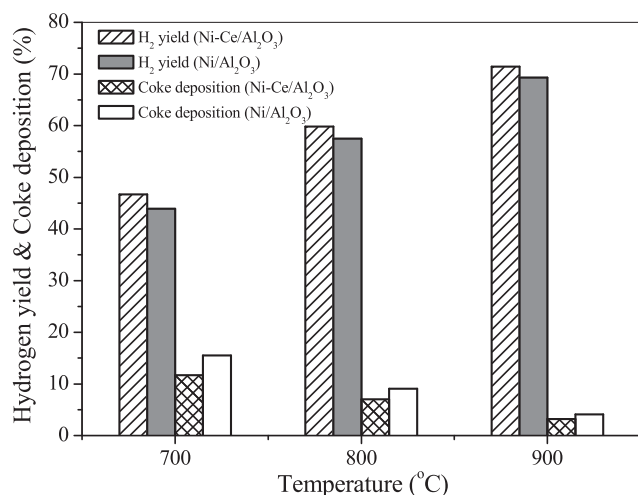


**Fig. 4 – Comparison of the activity of the four Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts with different Ni loadings at the operational conditions of  $\text{WCMR} = 6$  and  $\text{W}_{\text{bHSV}} = 12 \text{ h}^{-1}$ .**

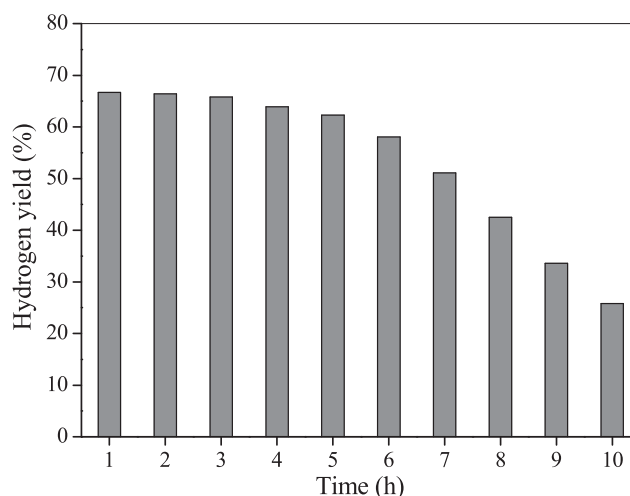
loadings, they show almost similar activities above 800 °C, indicating that the catalytic activity of the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts is not always enhanced by increasing the nickel loading. This is mainly because high nickel loadings may result in the aggregation of the nickel and/or blockage of the catalyst pores. It is noteworthy that the hydrogen yield for the NiCe-1 catalyst with the nickel loading of 5.1% was very close to those for the other three catalysts at 900 °C and at the same time, almost the same carbon conversions were obtained over all the catalysts. Above results suggest that the influence of nickel loading on bio-oil catalytic steam reforming is less pronounced at higher temperatures. Fig. 4 also reveals that the nickel loading does not have a major effect on the coke deposition percentage in the temperature range of 700–900 °C.

Based on the fact that NiCe-3 among the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> series was the best-performing catalyst from the perspective of hydrogen production, NiCe-3 and Ni/Al<sub>2</sub>O<sub>3</sub> with 14.9% Ni loading were selected for the further investigation on the effect of adding cerium as a promoter on steam reforming of bio-oil. Fig. 5 exhibits the influence of adding cerium promoter on hydrogen yield and coke deposition percentage. By adding the cerium promoter, the hydrogen yield is increased by almost 2.8%, 2.3% and 2.1% at 700, 800 and 900 °C, respectively. The coke deposition percentage is decreased by 3.8% at 700 °C by adding the cerium promoter, whereas it is decreased by only 0.9% at 900 °C. The above results show that the addition of a small amount of cerium promotes hydrogen production and improves the catalyst coking resistance. This is probably because the addition of cerium increases active oxygen species on the nickel surface due to enhanced water adsorption and effective gasification, which is favorable for hydrogen production and the inhibition of coke formation. In addition, the incorporation of cerium lowers the dissolution and diffusion of carbonaceous species through nickel particles and restrains the formation of carbon filaments [22].

The activity of the Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts was tested for 10 h to study their stability in the steam reforming of bio-oil. Fig. 6 shows the hydrogen yield as a function of reaction



**Fig. 5 – Comparison between the activities of NiCe-3 and Ni/Al<sub>2</sub>O<sub>3</sub> with 14.9% Ni loading in terms of hydrogen production and coke deposition percentage at various temperatures.**

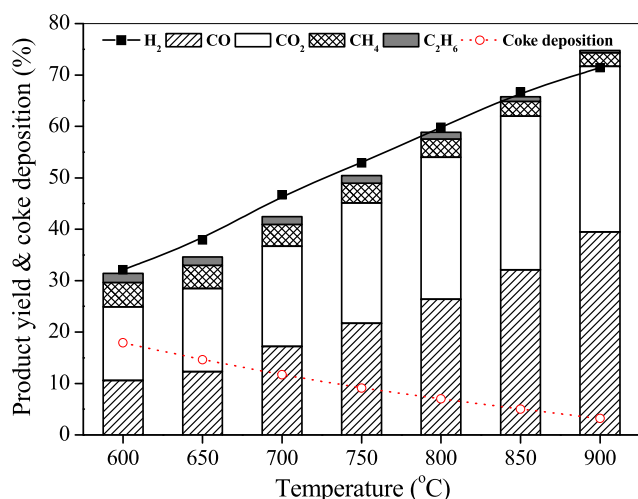


**Fig. 6 – Hydrogen yield as a function of reaction time over NiCe-3 catalyst at WCMR = 6, W<sub>b</sub>HSV = 12 h<sup>-1</sup> and temperature = 850 °C.**

time over NiCe-3 catalyst at WCMR = 6, W<sub>b</sub>HSV = 12 h<sup>-1</sup> and temperature = 850 °C. A gradual but slow deactivation is observed in the range of 0–6 h, corresponding to the slow decrease of hydrogen yield. A great and fast deactivation occurs with the further increase of reaction time, resulting in the sharp decrease in hydrogen yield. The reduced activity is mainly due to carbon deposition on the catalyst surface, which leads to the blockage of the catalyst pores and active sites.

#### Effect of reaction temperature

Temperature is a very important parameter influencing catalytic steam reforming of bio-oil. The yields of hydrogen and the main carbon-containing gaseous products (CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) as a function of temperature are presented in Fig. 7. The hydrogen yield is enhanced by increasing reaction temperature from 600 °C to 900 °C. The CO yield increases with the rise of reaction temperature. It is well known that the water gas shift reaction (WGS) is endothermic and the WGS moves towards the reverse direction of CO formation by increasing the reaction temperature, resulting in the increase of CO yield. The yield of CO<sub>2</sub> shows the similar trend to that of CO. This observation was also reported by Salehi et al. [23] when they tested Ru–Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for bio-oil steam reforming in the temperature range of 750–950 °C. The yields of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> always decrease with increasing temperature. When the temperature rises from 600 °C to 900 °C, the carbon conversion increases, but its increment is less pronounced than that of hydrogen yield. It is observed that the carbon conversion does not reach 100% even at 900 °C. The difference relates to the carbonaceous materials deposited on the catalyst bed, the carbon-containing products such as C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub> etc. that are difficult to be determined and the unconverted reactant itself. Wu et al. [14] studied the bio-oil catalytic steam reforming over the Ni/MgO catalyst in the temperature range of 700–900 °C and found that the deposited coke still existed on the catalyst surface even at 900 °C, which resulted in the carbon conversion less than 100%.

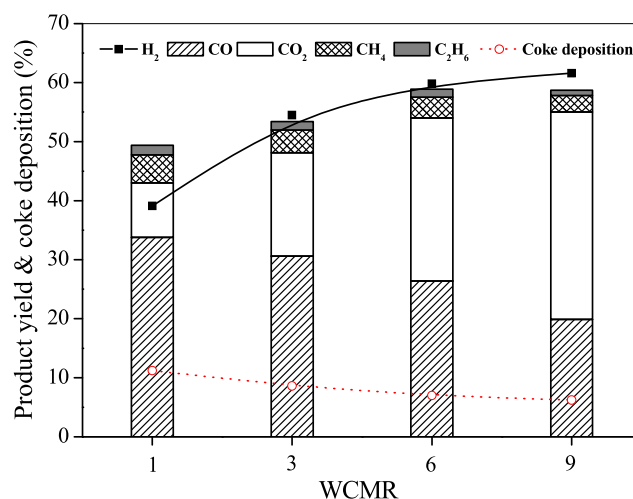


**Fig. 7 – Effect of reforming temperature on the yields of hydrogen and the main carbon-containing gaseous products as well as coke deposition percentage over NiCe-3 at the operational conditions of WCMR = 6 and  $W_b\text{HSV} = 12 \text{ h}^{-1}$ .**

Coke deposition, which is one of the main drawbacks in the catalytic steam reforming of bio-oil, could result in not only the decrease of hydrogen yield but also the catalyst poisoning or deactivation and reactor blockage. Thus the avoidance or inhibition of coke formation is very important. Fig. 7 also exhibits the coke deposition percentage as a function of temperature over the NiCe-3 catalyst. The decrease in the coke deposition percentage is achieved by increasing the temperature. The coke formation may be mainly attributed to the thermal decomposition of bio-oil and reaction intermediates, Boudouard reaction and carbon oxides reduction reactions. Iojoiu et al. [24] reported that bio-oil organic components were firstly thermally cracked to small molecular gases and coke deposition on the catalysts during bio-oil catalytic steam reforming. This was mainly ascribed to high thermal instability of biomass pyrolysis oil. Rennard et al. [25] pointed out that coke formation can be attributed to the dehydration and polymerization of aromatic and unsaturated components in biomass pyrolysis oils.

#### Effect of WCMR

The WCMR could be adjusted by changing the bio-oil feeding rate and water feeding rate. Fig. 8 exhibits that the influence of the WCMR on the yields of hydrogen and the main carbon-containing gaseous products (CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) as well as coke deposition percentage. The hydrogen yield increases significantly from 39.1% to 61.6% with increasing the WCMR ratio from 1 to 3 and increases slightly with the further increase of the WCMR. The CO yield always decreases with increasing the WCMR. The opposite trend was observed for CO<sub>2</sub>. This is mainly because increasing the WCMR is conducive to the proceeding of WGS towards hydrogen production, leading to the continuous decrease of CO yield and the increase of H<sub>2</sub> and CO<sub>2</sub> yields. Domine et al. [16] studied the influence of the steam-to-carbon molar ratio (S/C) on hydrogen production from beech wood pyrolysis oils over



**Fig. 8 – Effect of WCMR on the yields of hydrogen and the main carbon-containing gaseous products as well as coke deposition percentage over NiCe-3 at the operational conditions of temperature = 800 °C and  $W_b\text{HSV} = 12 \text{ h}^{-1}$ .**

monolithic platinum- and rhodium-based catalysts and found that the hydrogen yield almost increased with increasing the S/C ratio from 0.5 to 10 over the Pt catalyst; whereas, over Rh-based catalyst, the hydrogen yield did not change much when the S/C ratio was greater than 2.5. Azad et al. [26] investigated bio-oil catalytic steam reforming for hydrogen production over Ni-supported alumina catalysts and found that the hydrogen yield was enhanced by increasing the S/C ratio from 1 to 2, whereas it leveled off by further increasing the S/C ratio. In addition, it is observed that the CO/CO<sub>2</sub> ratio significantly decreases when the WCMR increases from 1 to 9. At the same time, the coke deposition percentage always decreases.

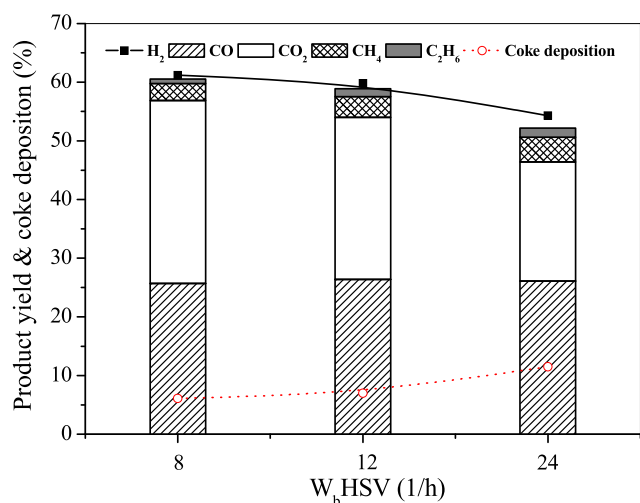
#### Effect of $W_b\text{HSV}$

The influence of  $W_b\text{HSV}$  on the H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> yields is presented in Fig. 9. Increasing the  $W_b\text{HSV}$  results in decreasing the residence time of the reactants on catalyst bed thus decreasing the bio-oil catalytic steam reforming efficiency. As a result, more reactants remain unconverted, which may condense with extra water or leave the system with exit gases. Consequently, the hydrogen yield decreases when the  $W_b\text{HSV}$  increases. At the same time, the coke deposition percentage changes little with increasing  $W_b\text{HSV}$  up to the value of 12 h<sup>-1</sup>, and then it increases by 4.5% with the further increase of  $W_b\text{HSV}$  from 12 to 24 h<sup>-1</sup>.

## Conclusions

Hydrogen production via catalytic steam reforming of maize stalk fast pyrolysis bio-oil over the nickel/alumina supported catalysts promoted with cerium was studied using a laboratory scale fixed bed coupled with Fourier transform infrared spectroscopy/thermal conductivity detection analysis. The effects of nickel loading, reaction temperature, water to carbon molar ratio and bio-oil weight hourly space velocity on





**Fig. 9 – Effect of  $W_b\text{HSV}$  on the yields of hydrogen and the main carbon-containing gaseous products as well as coke deposition percentage over NiCe-3 at the operational conditions of temperature = 800 °C and WCMR = 6.**

hydrogen production were investigated. A relatively high hydrogen yield over Ni–Ce/Al<sub>2</sub>O<sub>3</sub> catalysts was achieved by the bio-oil steam reforming. The highest hydrogen yield of 71.4% was obtained over the 14.9%Ni–2.0%Ce/Al<sub>2</sub>O<sub>3</sub> catalyst under the steam reforming conditions of temperature = 900 °C, WCMR = 6 and  $W_b\text{HSV}$  = 12 h<sup>−1</sup>. The effects of temperature and WCMR on the steam reforming process were very significant. Increasing reaction temperature from 600 °C to 900 °C resulted in the gradually increase of hydrogen yield. The hydrogen yield was significantly enhanced by increasing the WCMR from 1 to 3, whereas it increased slightly by further increasing the WCMR. The hydrogen yield decreased with the increase of  $W_b\text{HSV}$ . At the same time, the coke deposition percentage changed little with increasing  $W_b\text{HSV}$  up to 12 h<sup>−1</sup> and then it increased by 4.5% with the further increase of  $W_b\text{HSV}$  from 12 to 24 h<sup>−1</sup>.

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